Interpreting Narrative Objectives for Biostimulatory Substances Using the Technical Approach for Developing California Nutrient Numeric Endpoints

California Central Coast Water Board April 2, 2009

Goals – The intent of this technical paper is to set screening criteria for use in the 2008 303(d) / 305 (b) Integrated Report that will protect aquatic life beneficial uses from the consequences of excessive nutrient enrichment, or "biostimulation". The listing decisions associated with biostimulation will involve a "weight of evidence" approach described as an alternative procedure to the binomial distribution in the SWRCB Listing Policy (SWRCB, 2004). This technical paper establishes an upper range for dissolved oxygen concentration, over which reference site oxygen concentrations rarely or never fall. It also establishes a level of "oxygen deficit", predicted by the California Nutrient Numeric Endpoint technical approach, that is protective for aquatic life. Finally, it establishes a screening criterion for nitrate concentration that will be used to identify water bodies that have aquatic life impairments associated with biostimulation.

Background - The Central Coast Basin Plan currently contains narrative language stating that "waters shall not contain biostimulatory substances in concentrations that promote aquatic growths to the extent that such growths cause nuisance or adversely affect beneficial uses." Excessive nutrient concentrations stimulate algal growth, which can create nuisance conditions for water use and recreation, but more importantly, can remove oxygen from water, creating conditions unsuitable for aquatic life. Some algal blooms are also toxic to aquatic life, wildlife, and even humans. Waters that contain excessive algal growth are characterized by wide swings in dissolved oxygen concentrations, typically dropping below concentrations set to protect for aquatic life at night, and often rising above fully saturated levels during mid-day.

The State Water Resources Control Board funded development of the California Nutrient Numeric Endpoint (NNE) technical approach (Creager, et al., 2006) to interpret the biostimulatory narrative objective, and to support development of numeric criteria for nutrients to protect for aquatic life beneficial uses. The California NNE technical approach utilizes predicted benthic algae biomass and chlorophyll *a* concentrations as "response variables" to define Beneficial Use Risk Categories that can serve as preliminary numeric targets. These numeric targets are set at a conservative level to account for uncertainty and to be applicable throughout California. The NNE approach sets 200 mg chlorophyll *a*/ square meter as the level above which risk of impairment by nutrients is probable in warm water streams, and 150 mg/m2 as the level at which risk is probable in cold water streams. It also sets 80 grams/m2 ash free dry weight (AFDW) for algal density in warm water streams and 60 grams/m2 AFDW for algal density in cold water streams.

The California NNE provides background support for use of the associated California Benthic Biomass Spreadsheet Tool, to predict in-stream benthic algal density and other metrics in response to a number of inputs. The Biomass Tool utilizes data inputs for nutrient concentrations, as well as for latitude, canopy cover, stream depth and velocity to generate several model outputs. These include predicted benthic biomass and benthic chlorophyll *a* concentrations for both cold and warm water streams. It predicts these outputs for seven different models taken from the scientific literature. It also predicts the anticipated maximum oxygen deficit resulting from biostimulation. This is the maximum amount of dissolved oxygen expected to be removed from the water as a result of predicted algal growth. This latter value is calculated by EPA's revised QUAL2K model.

The Water Quality Control Policy (WQCP) for developing California's Clean Water Act (CWA) Section 303(d) list (SWRCB, 2004) describes the process by which the State Water Board and Regional Water Boards will comply with the listing requirements of Section 303(d) of the federal CWA. Section 6.1.3 "Evaluation Guideline Selection Process" provides the requirements for a proposed guideline to meet before it can be accepted as part of the 303(d) listing process. According to State Board staff analysis, the California NNE does meet these requirements, namely it is:

- Applicable to the beneficial use
- Protective of the beneficial use
- Linked to the pollutant under consideration
- Scientifically-based and peer reviewed
- Well described, and
- Identifies a range above which impacts occur and below which no or few impacts are predicted.

<u>Establishing Oxygen Reference Range</u> – Central Coast Water Board staff evaluated Central Coast Ambient Monitoring Program (CCAMP) diurnal oxygen data collected from 105 sites where probes had been deployed for a 24-hour period during summer months. CCAMP collects this data to determine if oxygen is depleted during the highest risk time of day, which is pre-dawn. This is important because staff conducts routine monthly grab sampling between 9 a.m. and 4 p.m., when oxygen levels are highest.

From the diurnal data, staff established two sets of potential oxygen reference data. The first reference data set consisted of the 32 sites where dissolved oxygen concentrations never dropped below 7.0 mg/L, the cold water aquatic life standard. The second consisted of the 59 sites where dissolved oxygen concentrations never dropped below 5.0 mg/L, the warm water aquatic life standard. We examined oxygen concentrations of both diurnal and monthly grab sample data for these sites for each hour of the day (Figures 1 and 2). For the 32 cold water sites, 29 sites never exceeded 13 mg/L at any time. Of the 644

grab samples taken at these cold water oxygen reference sites, only 6 (or 1.0%) samples exceeded 13 mg/L. For the 59 warm water sites, 43 sites never exceeded 13 mg/L at any time. Of the 1695 grab samples taken at these warm water oxygen reference sites, only 32 (or 1.9%) samples exceeded 13 mg/L. Staff has determined that 13 mg/L is an appropriate upper range value to screen both warm and cold water sites for oxygen super-saturation.

Central Coast Water Board Application of the California NNE - Central Coast Water Board staff has several goals in utilizing the California NNE for the 2008 303(d)/305(b) Integrated Assessment. The current Basin Plan nitrate criterion is set to protect drinking water for human health purposes. For many years, Central Coast staff has worked with staff from State Board and other Regions to support the development of nutrient criteria and the NNE, to provide us with a tool to protect against biostimulation. CCAMP data was utilized in development of the NNE. The NNE tool is now in place, and it is our goal to screen our highest priority water bodies during the 2008 listing cycle, with the intent of further evaluating this approach over the next two years for development of Basin Plan objectives and for screening of all water bodies for the 2010 Integrated Assessment.

Staff submitted CCAMP data (1998 – 2006) for water body minimums, maximums, and means for nitrate, nitrite, ammonia, ortho-phosphate, total phosphorus and water temperature into the California Benthic Biomass Tool. To screen data for probable effects, we utilized the NNE warm water threshold values of 200 mg/m² for chlorophyll *a* and 80 grams/m² ash-free dry weight (AFDW) for algal density, and the cold water threshold values of 150 mg/ m² for chlorophyll *a* and 60 grams/m² AFDW for algal density. We used default values for other model inputs, including latitude of 35 degrees, canopy cover of 80%, stream velocity of 0.3 meters per second and stream depth of 0.5 meters. Our assumption of a relatively dense canopy cover produces an estimate of probable effects that conservatively identifies problem conditions. Resulting outputs provided estimates of biomass and chlorophyll *a* production based on input variables, and also estimated oxygen deficit for each water body.

<u>Predicted Oxygen Deficit – Staff</u> evaluated resulting site outputs from the Biomass Tool for all CCAMP data. For each site, the Biomass Tool generated an estimated oxygen deficit for each site, based on predicted algal biomass. Almost five percent of CCAMP sites with a predicted oxygen deficit of 1.25 mg/L (or lower) had average dissolved oxygen concentrations below the Basin Plan standard of 7.0 mg/L (Figure 3). Staff asserts that an oxygen deficit of 1.25 mg/L represents an acceptable level of protection for aquatic life; it means that 95% of sites with no more than this level of oxygen deficit will meet the Basin Plan objective on average. The average Nitrate concentration which predicts this level of oxygen deficit is 1.0 mg/L (Figure 4). Staff have used 1.0 mg/L nitrate as N as a screening value to protect for aquatic life. This value will be further evaluated

by Basin Planning staff over the next two years for use as a Basin Plan objective and for future listing evaluations.

<u>CCAMP Data Confirmation of NNE Findings</u> – Staff evaluated CCAMP data for characteristics of sites meeting warm and cold water oxygen objectives that in staff's opinion do not show evidence of biostimulation. These sites fell within the oxygen reference ranges described above, and also met several other criteria. These were: water column chlorophyll a under 15 mg/L (the screening value used for 303(d) listing), filamentous algal cover never exceeding 50% of the water's surface, and overall algal cover not exceeding 95%.

No sites from the cold water data set, and only one site from the warm water data set had predicted oxygen deficits over 1.25 mg/L (Figures 5 and 6). In addition, no sites from the cold water data set and only one site from the warm water data set fell above 1.0 mg/L nitrate (as N) as an average (Figures 7 and 8). Staff concur that these findings support the numeric thresholds established through NNE.

<u>Using Nitrate Screening Criterion to Develop Lines of Evidence – Nitrate and other nutrients are treated as "toxins" by the Listing Policy (SWRCB, 2004).</u>
Consequently, staff evaluated nitrate potential for biostimulation using the binomial distribution established for toxic pollutants, in spite of the fact that it is being considered here as a biostimulant, not a toxin...Staff recommend that this be reconsidered in the Policy for future listings. Lines of Evidence were developed based on exceedance of 1.0 mg/L Nitrate (as N). Staff provided further evidence of biostimulation using supporting data and NNE model outputs. These include predictions of algal biomass and/or chlorophyll *a* concentrations exceeding model thresholds for warm and cold water habitat, evaluation of model prediction of oxygen deficit relative to thresholds established by staff, and/or evaluation of data for evidence of oxygen depression and/or super-saturation, which are both indications of biostimulation.

References

Creager, C., J. Butcher, E. Welch, G. Wortham, and S. Roy. July 2006. Technical Approach to develop Nutrient Numeric Endpoints For California. Tetratech, Inc. Prepared for U.S. EPA Region IX and State Water Resources Control Board.

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SWRCB. 2004. Water Quality Control Policy for Developing California's Section 303(d) List. Resolution No. 2004-0063. Sacramento, CA: State Water Resources Control Board. California Environmental Protection Agency.

SWRCB. December, 2007. Staff Report: Nutrient Screening Tools for Use in the Clean Water Act Section 303(d) Listing Process

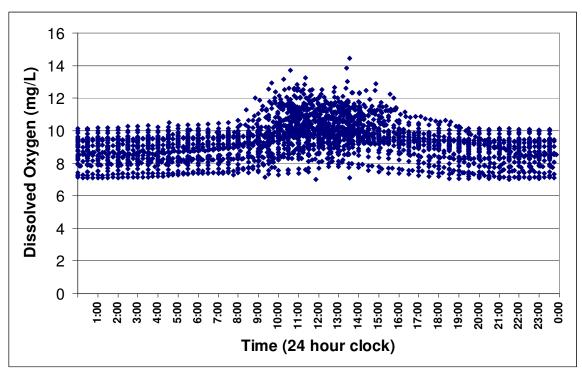


Figure 1. Hourly dissolved oxygen at cold water reference sites (CCAMP data, 1998-2008). Includes 24-hour probe and grab sample data.

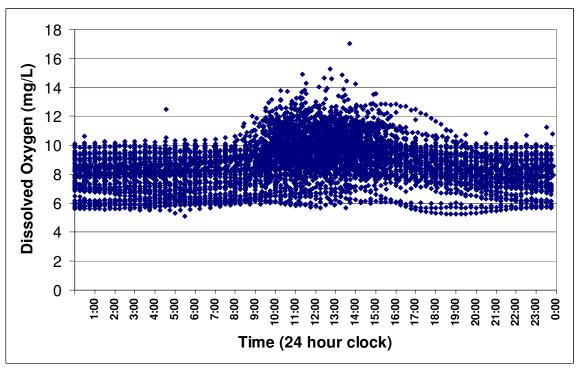


Figure 2. Hourly dissolved oxygen at warm water reference sites (CCAMP data, 1998 – 2008). Includes 24-hour probe and grab sample data.

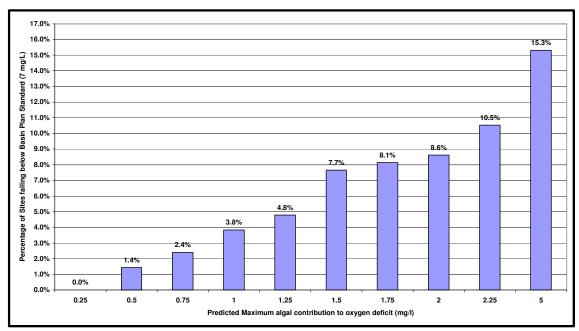


Figure 3. Percentage of CCAMP sites currently falling below the Basin Plan oxygen objective of 7.0 mg/L, and their predicted oxygen deficit attributable to algal biomass. At an oxygen deficit of 1.25 mg/L, approximately 5% of sites have average oxygen concentrations below the Basin Plan standard.

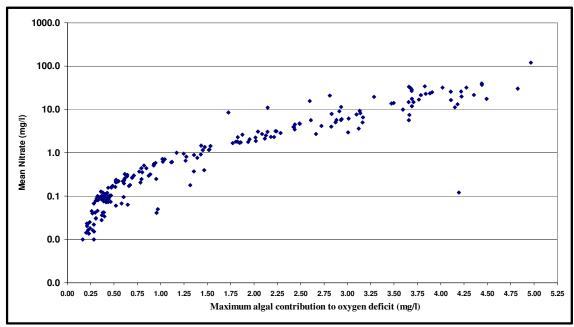


Figure 4. Relationship between average site nitrate concentrations (as N) and predicted oxygen deficit (mg/L). An average nitrate concentration of 1.0 mg/L predicts an estimated maximum algal contribution to oxygen deficit of 1.25 mg/L, based on the California NNE.

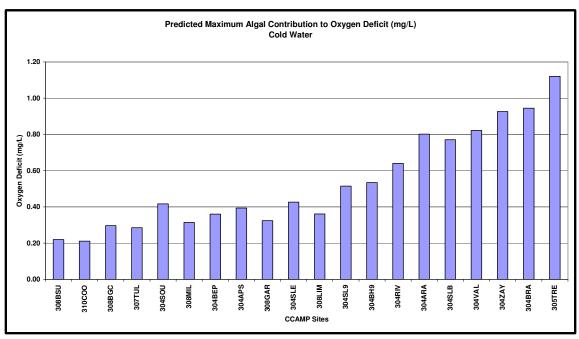


Figure 5. Predicted Maximum Algal Contribution to Oxygen Deficit (mg/L) for CCAMP sites that never violate the Cold Water Oxygen Objective (7 mg/L) and that do not exceed several screening criteria for indicators of biostimulation.

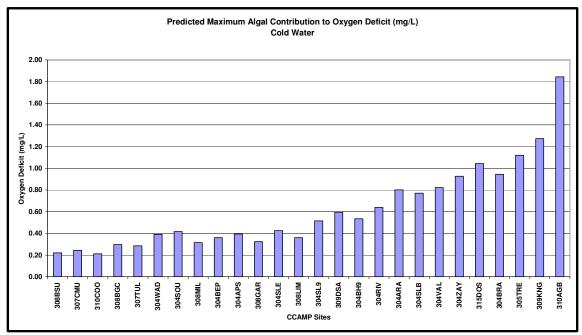


Figure 6. Predicted Maximum Algal Contribution to Oxygen Deficit (mg/L) for CCAMP sites that never violate the Warm Water Oxygen Objective (5 mg/L) and that do not exceed several screening criteria for indicators of biostimulation.

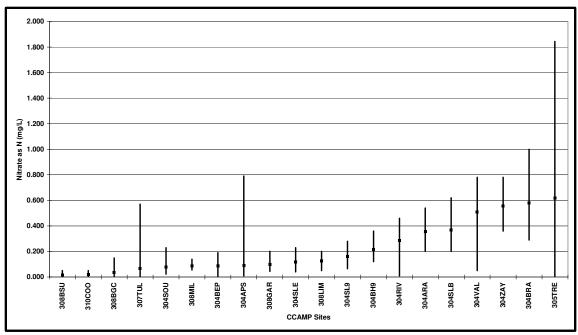


Figure 7. Mean Nitrate concentrations (mg/L) at CCAMP sites that never violate the Cold Water Oxygen Objective (7 mg/L) and that do not exceed several screening criteria for indicators of biostimulation.

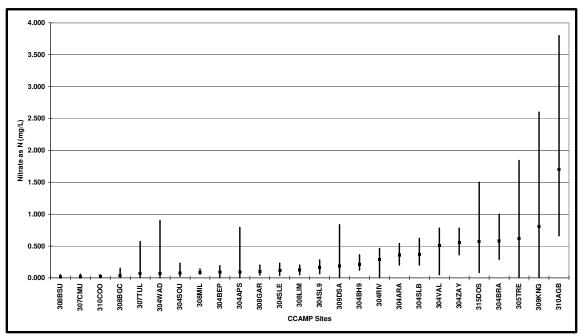


Figure 8. Mean Nitrate (as N) concentrations (mg/L) at CCAMP sites that never violate the Warm Water Oxygen Objective (5 mg/L) and that do not exceed several screening criteria for indicators of biostimulation.